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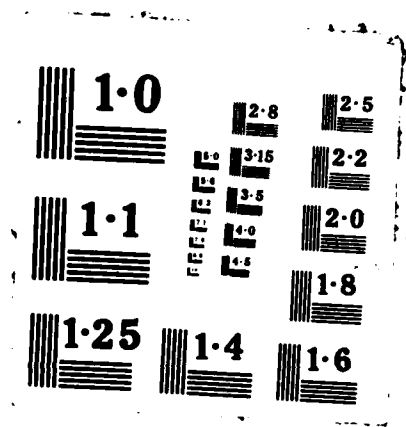
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SYNTHESIS AND CHARACTERIZATION OF 1,2-DISUBSTITUTED
CYCLOBUTENE AMIDES: POLYMERS AND CYCLOADDUCTS

by

Lon J. Mathias and Douglas G. Powell

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A series of model diamides were synthesized from mono- and disubstituted amines with the diacid chloride of cyclobutene-1,2-dicarboxylic acid. Yields ranged from 30 to 70%. Melting points of the purified diamides ranged from less than 239°C for N-alkyl and N,N-dialkyl species to 204°C for the N-phenyl model. Relative rates of thermolysis (by DSC) with maxima from 208-224°C at 10°C/min. were dependent on the number and type of substituents, and intramolecular hydrogen bonding. Thermolysis products were Diels Alder dimers (for N-mono-substituted materials and for bulky tetrasubstituted models) while polymers formed spontaneously for two tetrasubstituted models with at least one methyl group on each nitrogen. Thermal imidization of cycloadducts was possible in some cases with concomitant oxidation to tetrasubstituted aromatic bisimides.					
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SYNTHESIS AND CHARACTERIZATION OF 1,2-DISUBSTITUTED CYCLOBUTENE AMIDES: POLYMERS AND CYCLOADDUCTS

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INTRODUCTION

2,3-Disubstituted cyclobutenes and their corresponding butadienes display a rich variety of addition reactions. The cyclobutenes can react via cycloaddition with appropriate dienes while the butadienes have been found to dimerize and polymerize as well as undergo typical [4 + 2] cycloadditions.

Recently, we reported the synthesis of diamides and polyamides based on cyclobutene-1,2-dicarboxylic acid to generate monomers and polymers with nascent butadiene functionality.¹ The cyclobutene moiety of such compounds generally undergoes thermal ring-opening above 180°C to form the corresponding 2,3-disubstituted butadiene.

We are currently exploring these compounds for synthesis of novel polybutadienes and for curing of thermosetting polymers and composites. Understanding the chemical behavior of the cyclobutene functionality in these systems is essential to evaluation of the composite cure process and final product performance.

We previously described our initial results on thermal reactions of some model diamides (1-3) and polyamides. Spontaneous polymerization occurred only for 2 while the others cyclodimerized. In an effort to better understand the factors controlling the spontaneous reactions of these butadienes, a number of additional derivatives (4-9) have been synthesized and their properties and behavior examined. We report here the general synthesis of these model compounds, their thermal reaction energetics, and their reaction products.

EXPERIMENTAL

Facile synthesis of model amides was accomplished by reacting appropriate monofunctional amines with the intermediate cyclobutene-1,2-diacid chloride. The general synthesis was described previously¹ and extended to derivatives 4-7. ¹³C NMR high-resolution and solid-state spectra were obtained on a Bruker MSL 200 spectrometer at a frequency of 50.32 MHz. Chemical shifts are reported in ppm from TMS (0 ppm). Thermal analysis was performed on a DuPont 910 Differential Scanning Calorimeter. Composition of the model compounds was confirmed by microanalysis (Desert Microanalysis, Tuscon, Arizona). Isolated yields, melting points, and ¹³C NMR chemical shifts are given in Table 1.

RESULTS AND DISCUSSION

Thermal Analysis by DSC

DSC was used to investigate the onset and breadth of various thermally induced transitions and reactions, and to determine the enthalpy of the individual processes. Table 2 lists the values for melting points determined by DSC, the exotherm maxima (T_{max}), and enthalpies for the peaks. For a given scan rate, the position of the maximum of a specific peak is an indication of the relative reaction rate.²

For the cyclobutene ring-opening process, T_{max} varies less than 20°C for the series of derivatives 1-9. Cyclobutenes substituted in the 3-position, however, show a wide range of thermolysis rates that are strongly dependent on the type of

substituent.³ Alkyl and aryl substituents on the amide nitrogen may be too far removed from the ring to exert more than nominal influence on ring-opening energetics.

The presence of intramolecular hydrogen bonding in the model amides, however, exerts a much stronger influence. Comparison of compounds 3-6 and 8 reveals almost identical T_{max} independent of the R substituent. In the series, the relative rate of reaction decreases in the order N-alkyl > N-aryl > N,N-dialkyl > N-alkyl-N-aryl > N,N-diaryl. Hydrogen bonding increases the rate while aryl substituents decrease it.

Table 2. Thermal Analysis Results by DSC.

Cmpd	T _m (°C)	T _{max} (°C)	ΔH _t (kcal/mole)
1	186.2	224.2	13.6
2	151.8	220.6	20.5
3	202.5	(211) ^a	----
4	72.0	208.3	11.4
5	56.4	208.2	23.2
6	--- ^b	208.2	17.4
7	--- ^b	214.5	24.6
8	156.0	208.2	14.7
9	183.6	228.4	21.4

^aPeak obscured by melt endotherm

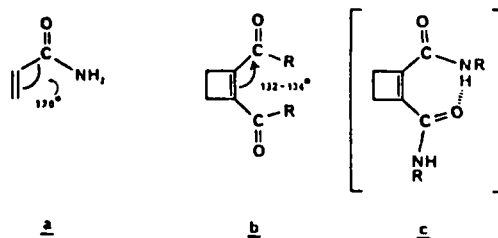
^bViscous oils at room temperature

The experimental heats of reaction (ΔH_t) vary widely but do not appear to relate to the number or type of substituents. This probably results from the DSC exotherms being combinations of two or more reactions: ring-opening followed by either or both polymerization and cycloaddition. Indeed, compounds 4-6 show two overlapping exotherms clearly demonstrating the consecutive nature of these reactions. These three compounds undergo almost exclusive cycloaddition while 2 and 7 give only polymeric products. DSC scans of 2 and 7 show only one exotherm peak. The appearance of a single peak is not exclusive to polymer formation, however, since compound 1 shows only one peak yet undergoes only cycloaddition. The appearance of a bimodal exotherm, or lack of one, may simply be due to the difference in the rate of ring-opening and subsequent reactions.

Polymerizability

The polymerizability of the butadiene compounds may be directly related to the occurrence of intramolecular hydrogen bonding in both the cyclobutene and the butadiene. Although the 7-membered cyclic structure required for the hydrogen bond in the former may at first appear strained, the large angle of the sp² hybridized carbons of the ring actually favor this structure (Figure 1a-c).⁴

Figure 1



A similar structure has been confirmed by X-ray analysis of cyclobutene-1,2-dicarboxylic acid and invoked to explain its unusual cycloaddition behavior.⁵ The solid state ¹³C NMR of 3 is shown in Figure 2 along with the proposed intramolecular



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